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Dynamic mechanical studies of the glass transition temperature of photopolymerized multifunctional acrylates

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Summary

The glass transition temperatures of the highly crosslinked networks formed from photopolymerizing the multifunctional monomers trimethylol propane triacrylate (TrMPTrA), pentaerythritol tetraacrylate (PETeA), and dipentaerythritol monohydroxy pentaacrylate (DPEMHPeA) were determined using a dynamic viscoelastometer. All glass transition temperatures, T_g, were in excess of 150°C indicating the highly crosslinked structure of the resulting networks. The curves of the damping factor as a function of temperature were broadened peaks spanning up to 100°C due to the extreme heterogeneity of these structures. Evidence of trapped radicals was also observed as cured samples subjected to a thermal pretreatment had higher T_g than those without the thermal pretreatment.

Introduction

Photopolymerization of multifunctional monomers results in densely crosslinked networks that have increased thermal and dimensional stability. These physical properties along with the rapid curing rates of photopolymerization have made these materials candidates for applications in fiber optic coatings, laser video discs, aspherical lenses, and dental restorative materials (1-7). Since thermal and dimensional stability are directly related to the degree of crosslinking, the glass transition temperatures of a series of polyacrylates (tri, tetra, and penta) were measured to determine if increasing functionality increased the degree of crosslinking.

In general, photopolymerization of multifunctional monomers at ambient temperatures results in densely crosslinked glassy polymer networks with incomplete functional group conversion (1,2,8). This incomplete conversion of the multifunctional monomer relates to the early onset of vitrification which significantly decelerates the reaction rate. To achieve higher conversion, the mobility of the molecular species during reaction must be increased. This can be achieved by raising the reaction temperature (provided degradation does not occur), decreasing the crosslinking density (by increasing the chain length between functional groups), increasing the rate of reaction (which generates excess free volume), or adding an appropriate solvent.

Trapping of radicals in glassy polymer networks during polymerization is another well established phenomenon which has been studied extensively with electron spin resonance (ESR) spectroscopy. Researchers have observed that photopolymerized dimethacrylates stored at room temperature and under vacuum have radical lifetimes exceeding 5 months. These extended lifetimes persist even when large amounts of monomer and unreacted functional groups are present (9). Others have shown the dependence of radical lifetimes on the crosslinking density (10).

Finally, inhomogeneities in the formation of crosslinked networks arise from the existence of localized regions of vastly differing mobilities. Differential scanning calorimetry (DSC) and ESR measurements for polydimethacrylate and polydiacrylate samples have shown trapping of radicals at the beginning, as well as at the end of the reaction (11). As temperature is increased in these systems, the network gains mobility, allowing further reaction and crosslinking of the system.

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Experimental

The multifunctional monomers selected for this study were trimethylol propane triacrylate (TrMPTrA, Aldrich Chemical Co., Milwaukee, WI), pentaerythritol tetraacrylate (PETeA, Sartomer, West Chester, PA), and dipentaerythritol monohydroxy pentaacrylate (DPEMHPeA, Sartomer, West Chester, PA). Monomer structures are shown in Figure 1. All monomers were used as received. The photoinitiator chosen for the ultraviolet polymerizations was 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich Chemical Co., Milwaukee, WI).

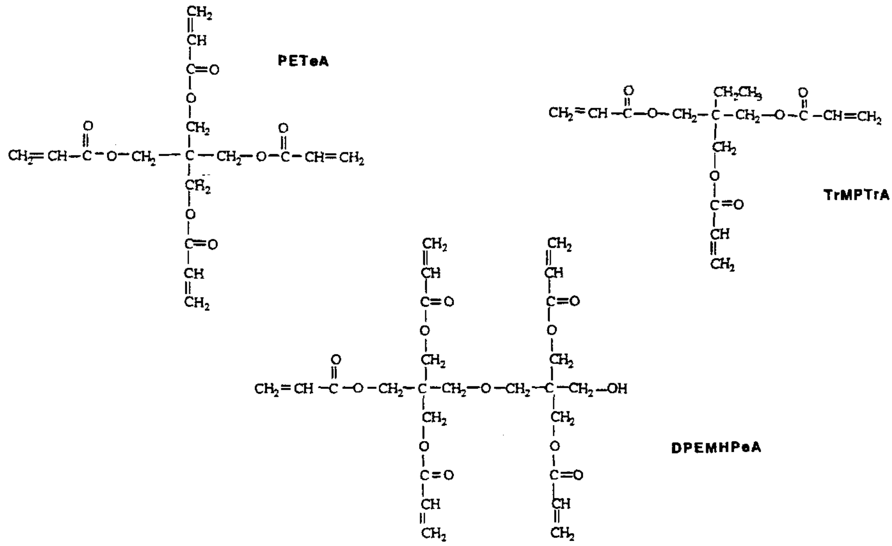

Figure 1. Multifunctional monomer structures.

Samples were prepared by placing approximately 3 cm^3 of monomer solution with 1 wt % DMPA in flat bottomed aluminum pans creating a coating approximately 1 mm thick. The samples were irradiated with an effective intensity (accounting for the radiation from the reflected beam) of 4 mW/cm^2 for 30 minutes. Polymerizations were conducted under a nitrogen atmosphere at temperatures ranging from 27-30°C with an Ultracure 100 (Engineered Fiber Optic Systems, Buffalo, NY) ultraviolet source.

Polymerized samples were stored for approximately one week under refrigeration in air before dynamic mechanical testing. The stored samples were then cut into rectangular strips 20-30 mm in length and 0.7-1.0 mm in width. A dynamic viscoelastometer (Rheovibron, DDV-II, Toyo Baldwin Co., Japan) monitored relative changes in the elastic to viscous moduli as temperature was linearly increased at the rate of 5°C/min. The glass transition temperature, T_g, range for each sample was then determined as the maximum in the damping factor. The samples of polyPETeA and polyDPEMHPeA were tested twice to check for post-curing of the polymer during the initial experiment when the sample was heated. The second experiment followed the first immediately after the sample was cooled to 50°C. Each experiment was conducted over the temperature range of 50°C to 250°C.

Results and Discussion

Determination of the glass transition temperature range for the various polymer networks provided insight into the crosslinking density, thermal stability, and mechanical stability of the final polymer structure. The polymer networks were characterized by dynamic mechanical methods rather than by DSC, since DSC lacks the sensitivity for detection of transitions in these heterogeneous, densely crosslinked polymers. Figure 2 shows the damping factor as a function of temperature for a sample of polyTrMPTrA. Figure 3 represents a sample of polyPETeA studied twice to check for further polymerization during the first experiment, and the same is true for polyDPEMHPeA in Figure 4.

All glass transition temperatures determined were greater than 150^{o}C: polyTrMPTrA (T_g>240^{o}C), polyPETeA (T_g=180^{o}C), polyDPEMHPeA (T_g=160^{o}C). These values were indicative of the densely crosslinked nature of the networks. Glass transition temperatures and ranges are reported for each network in Table 1. These high T_g's were also representative of the thermal and dimensional stability of these networks which is desired for the discussed applications.

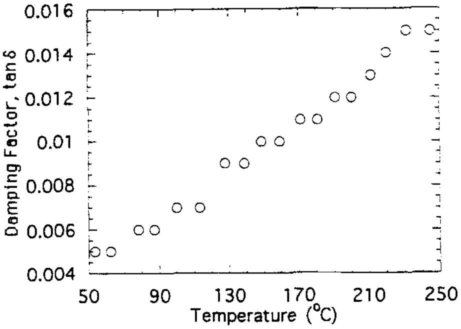

Figure 2. The damping factor as a function of temperature for polyTrMPTrA cured with 4 mW/cm^2 of UV light for 30 minutes.

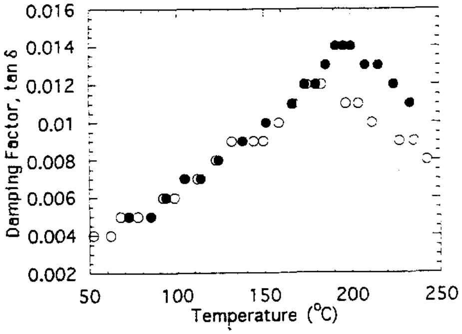

Figure 3. The damping factor as a function of temperature for polyPETeA cured with 4 mW/cm^2 of UV light for 30 minutes (o no thermal treatment and • after thermal treatment).

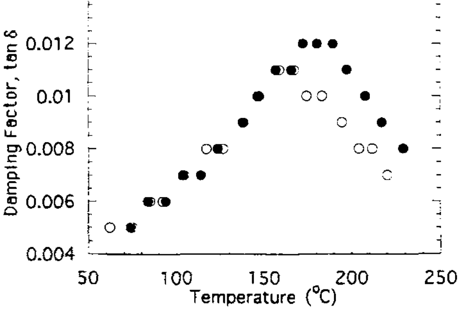

Figure 4. The damping factor as a function of temperature for polyDPEMHPeA cured with 4 mW/cm^2 of UV light for 30 minutes (o no thermal treatment and • after thermal treatment).

The data in Figures 2, 3, and 4 show trends in decreasing T_g ranges with increasing functionality of monomer (i.e. T_g (polytriacrylates) > T_g (polytetraacrylates) > T_g (polypentaacrylates)). Again, this is explained by the lower conversion of the more highly functional monomers. The lower conversions resulted in networks that were on average less densely crosslinked, despite the greater functionality, than the higher conversion networks. This trend in behavior is opposite of that seen for mono- and dimethacrylates (12), as increasing the functionality of the monomer increases the T_g range. This suggests that for a given set of curing conditions an optimum functionality exists, balancing high conversion and high functionality, that produces the highest average crosslink density.

Table 1
Glass Transition Temperature Ranges of PolyTrMPTrA, PolyPETeA and PolyDPEMHPeA

	Functionality	**Thermal Treatment**	T_g (°C)	T_g **Range (°C)**
polyTrMPTrA	6	No	>240	240 -
polyPETeA	8	No	175	170-185
polyPETeA	8	Yes	190	185-200
polyDPEMHPeA	10	No	160	155-170
polyDPEMHPeA	10	Yes	180	170-190

Focusing on Figure 3, the T_g range for polyPETeA was initially determined as 170-185°C. During the experimental procedure, the polymer sample was heated from room temperature to 250°C. Obviously, if free radicals were trapped in the polymer network, the significantly increased mobility at 250°C (above T_g) would allow further reaction. Therefore, the sample was allowed to cool in the sample chamber while exposed to the atmosphere, and then the experiment was repeated. The results show that the T_g range shifted to 185-200°C. Indeed, further crosslinking occurred, and this shift indicated that trapped radicals were present. The presence of trapped radicals, after more than a week in an oxygen environment, is also indicative of the highly crosslinked nature of these polymers. Oxygen is known to react with active radicals and form inactive species. Therefore, it is clear that oxygen diffusion through the polymer was severely limited during the week the samples were exposed, not allowing the active radicals to react with the oxygen.

Similar results are seen in Figure 4 for DPEMHPeA. The initial T_g range was 155-170°C, and the second experiment shows a shift in T_g to 170-190°C. Figure 2 differs from Figures 3 and 4 in that a definite maximum in tan δ is not observed. From the results, the glass transition temperature range had just been reached at the 240-250°C range, or the polymer had undergone degradation. This behavior is similar to that observed in highly crosslinked dimethacrylates (13).

Generally, for thermal polymerizations, the difference between the curing temperature and the glass transition temperature does not exceed 15-35°C (14-16). Our experimental results show differences in the glass transition temperature and the curing temperature for photopolymerization ranging from 150-200°C. Kloosterboer and Lijten (17) have reported differences up to 70°C for the ambient photopolymerization of 1,6-hexanediol diacrylate. One reason for this difference is the excess free volume created by the slow volume relaxation in photopolymerized systems, which adds mobility to the system. This is also coupled with the continued polymerization in the glassy state due to the presence of a significant amount of unreacted functional groups present even at high conversions for multifunctional monomers and the existence of reaction diffusion in the glassy network (18). Reaction diffusion occurs when trapped radicals "propagate" through the matrix of unreacted functional groups until encountering a second radical and terminating.

Photopolymerizations of multifunctional monomers at room temperatures lead to densely crosslinked, glassy networks with incomplete functional group conversion, high glass transition temperatures, and trapped radicals. As the functionality of the monomer is increased (di, tetra, hexa, octa, and deca), a maximum in T_g occurs. This suggests the existence of an optimum functionality, a balance between high conversion and high functionality, that produces the highest average degree of crosslinking. Finally, differences in the curing temperature and the glass transition temperature of these networks suggest the dominance of reaction diffusion as a reacting mechanism for free radicals in the gel and glassy state.

Acknowledgements

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